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LA-UR-13-????

Hydrodynamic Theory of Diffusion in Gases and Plasmas

C. H. Chang and H. J. Chang

Los Alamos National Laboratory

LANL

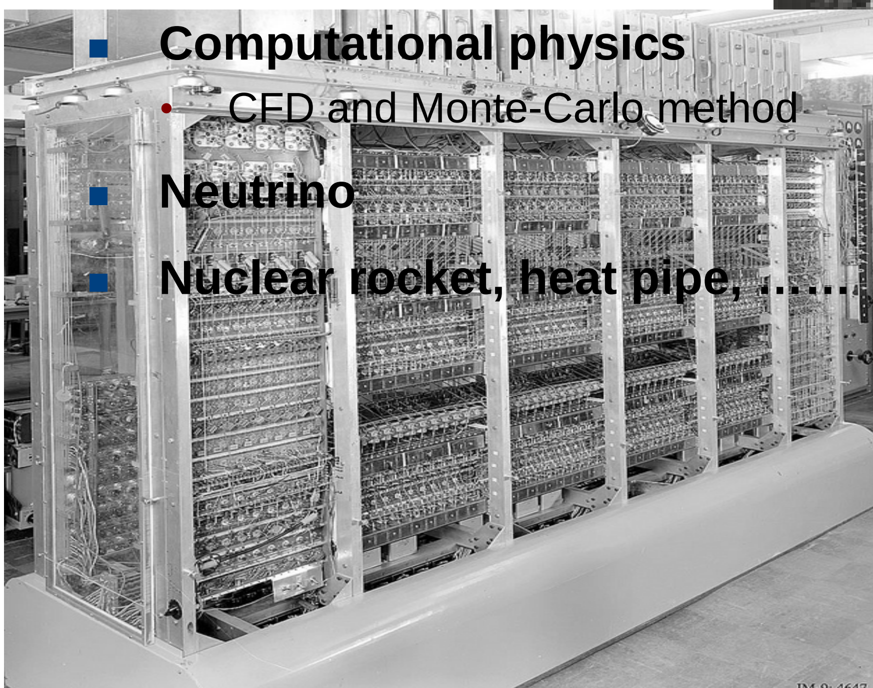
- **Located about 35 miles from Santa Fe, New Mexico**
- **36 square miles (~100 km^2)**
- **10,000+ employees**
  - 21% holds Ph.D.
  - 400+ Postdoctoral researchers
  - 800+ Students
- **$ 2.2 billion/year**

At the beginning

- **Started as the secret design laboratory of atomic weapon**
  - Operated by University of California
- **Oppenheimer, Feynman, Fermi, Bethe, Segre, Ulam, Von Neumann, Teller …**
- **Little Boy and Fat Man**

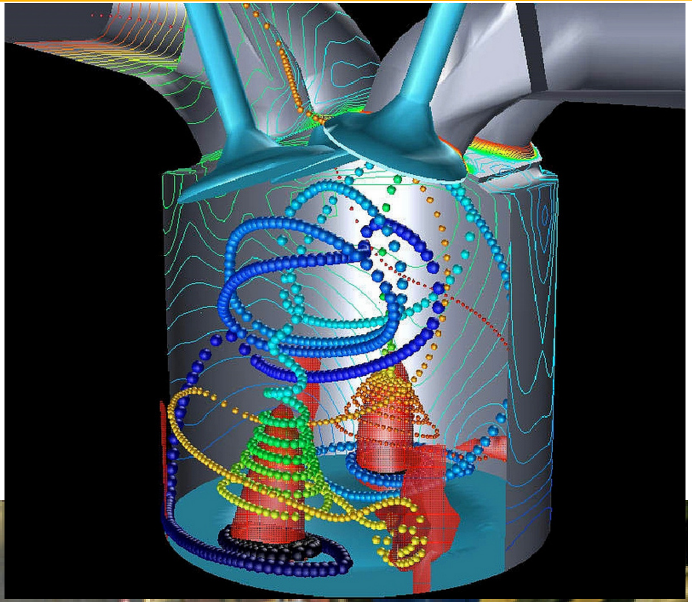
Cold war

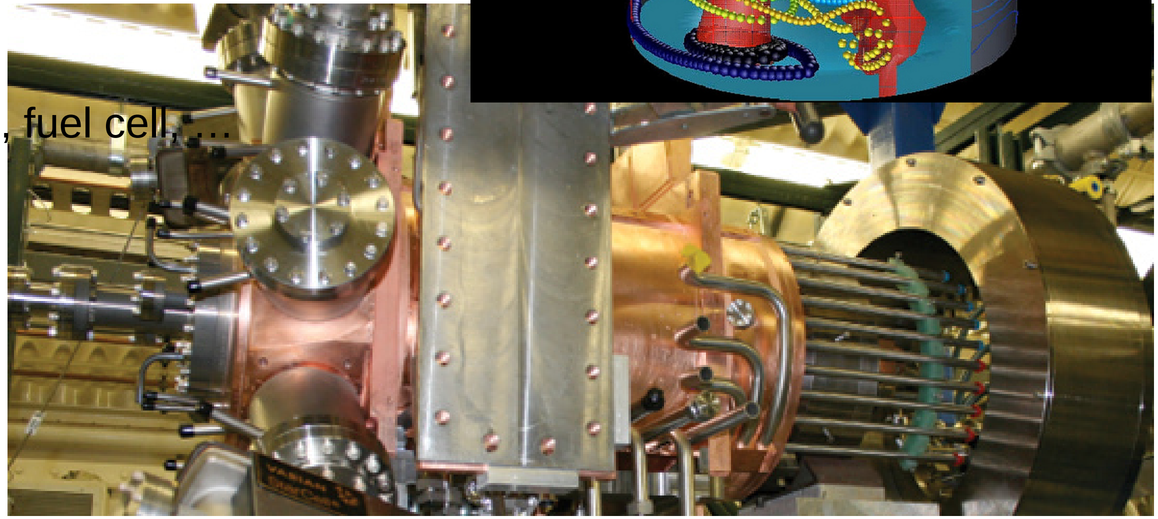
- **Thermonuclear weapon**
- **High-performance computing**
  - MANIAC
- **Computational physics**
  - CFD and Monte-Carlo method
- **Neutrino**
- **Nuclear rocket, heat pipe, ……**



Today

- **Test Moratorium and Stockpile Stewardship**
  - Numerical simulation
  - Experiment (DAHRT, ICF, …)
  - Aging
  - Pu science
- **Nonproliferation and threat reduction**
  - Forensics
- **Clean energy**
  - Renewable, wind, biofuel, fuel cell, …
- **HED, Plasmas, MHD, …**
- **Material Science**
- **Life science**





Acknowledgment

- **Theoretical research in collaboration with John D. Ramshaw.**
  - J. D. Ramshaw, J. Non-Equilib. Thermodyn. **15**, 295 (1990).
  - J. D. Ramshaw and C. H. Chang, J. Non-Equilib. Thermodyn. **21**, 223 (1996).
  - J. D. Ramshaw and C. H. Chang, Plasma Chem. Plasma Process. **12**, 299 (1992).
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  - J. D. Ramshaw and C. H. Chang, Phys. Rev. E **53**, 6382 (1996).
- **Thanks to Deepak Bose, Helen Hwang, Meyya Meyyappan, Joon-Hong Park, Emil Pfender, A. J. Scannapieco, Alan Stagg, and Les Thode at NASA Ames Research Center, Oak Ridge National Laboratory, University of Minnesota, Novellus Systems, and Los Alamos National Laboratory**

Topics covered

- **Issues in using Fick's law**
  - Use of multicomponent diffusion coefficient
  - Violation of mass conservation
- **Stefan-Mawell (SM) equations**
  - Use of binary diffusion coefficient
  - Mass conservation automatic
- **Extension of SM equations to diffusion in plasmas**
  - Charge neutrality
  - Multi-temperature mixture

Accurate modeling of diffusion in gas/plasmas important

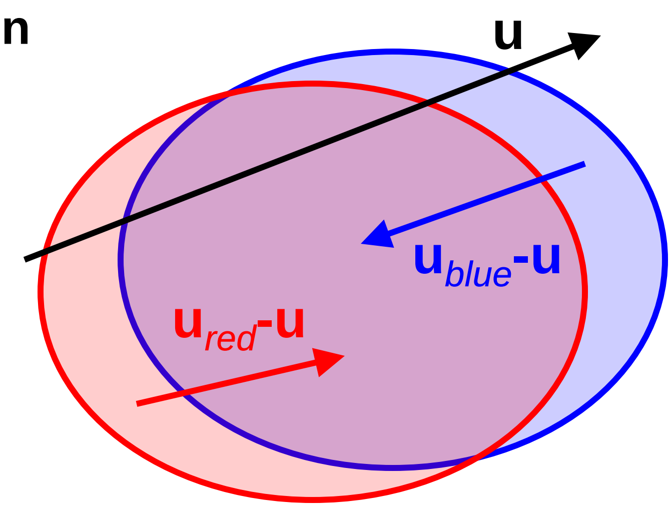
- **Combustion**
- **Etching and deposition in semiconductor processing**
- **Air plasma flow around re-entry vehicle**
  - The dominating heat transfer mechanism is recombination of ionized and dissociated species on the solid surface.
- **Materials processing using plasmas**
- **Presented formulations have been implemented and used by a number of research groups for simulations of:**
  - Multicomponent plasma jets discharging into air
  - Semiconductor processing
  - Electric discharges and arcs
  - Reactive flows

Fick's law

- **Fick's law frequently used for diffusion**

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{u}) = -\nabla \cdot \mathbf{J}_i$$

$$\mathbf{J}_i \equiv \rho_i (\mathbf{u}_i - \mathbf{u}) = \rho D_i \nabla c_i$$



- **Drift (diffusion) velocity = $\mathbf{u}_i$ – u**
- **Multicomponent diffusion coefficients** D_i
  - Determined from the kinetic theory
  - When N = 2, it becomes the binary diffusion coefficient
  - For multicomponent mixtures (N > 2), it depends on local composition.
- **Mass conservation not always satisfied for** N > 2

Mass conservation

- **Summing over all species should result in the continuity for all species**

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0, \qquad \sum_i \rho_i = \rho$$

- **This puts the constraint on mass flux,** $\sum_i \mathbf{J}_i = \mathbf{0}$
- **Computationally, we must satisfy**

$$\sum_i \rho_i \mathbf{u}_i = \rho \mathbf{u}_{\text{diffusion}} = \rho \mathbf{u}_{\text{momentum eq}}$$

  - Obtaining diffusion flux is determining species velocities u_i
  - u is obtained from the momentum equation

- **I.e., u from the sum of diffusion flux must be identical to the u obtained from the momentum equation**

- **This constraint is not automatically satisfied. The set of equations solved must satisfy this constraint.**

Properties of Fick's law

- **Mass conservation automatic when** $N = 2$
- **When** $N > 2$**, mass conservation satisfied only when** D_i **is the same for all** i
  - Unsatisfactory
  - Practice of solving diffusion equation for N - 1 species and obtaining Nth species diffusion flux using the mass conservation should be avoided
- **Self-Consistent Effective Binary Approximation (SCEBD) can be used for nonuniform** D_i
  - J. D. Ramshaw, J. Non-Equilib. Thermodyn. **15**, 295 (1990).
  - Still an approximation
- D_i **needs to be calculated for all species in every cell in each time step**
  - Dependency on concentration
  - Approximate evaluation method using binary diffusion coefficients (no concentration dependency) presented in:

    J. D. Ramshaw and C. H. Chang, J. Non-Equilib. Thermodyn. **21**, 223 (1996).

Stefan-Maxwell (SM) equations

- Independently proposed by Stefan and Maxwell
- Utilize more convenient binary diffusion coefficient D_{ij}, not D_i
- Derivation presented in Appendix of F. A. Williams, Combustion Theory, 2nd ed. (Addison-Wesley, Redwood City, CA 1985)
- Williams also discussed why SM equations are preferred over Fick's law with multicomponent diffusion coefficients
- Alternate derivation using the Hydrodynamic Theory of Diffusion presented here – EASY!! Do not panic.

SM equations from hydrodynamic theory

- **We start from species momentum equations**

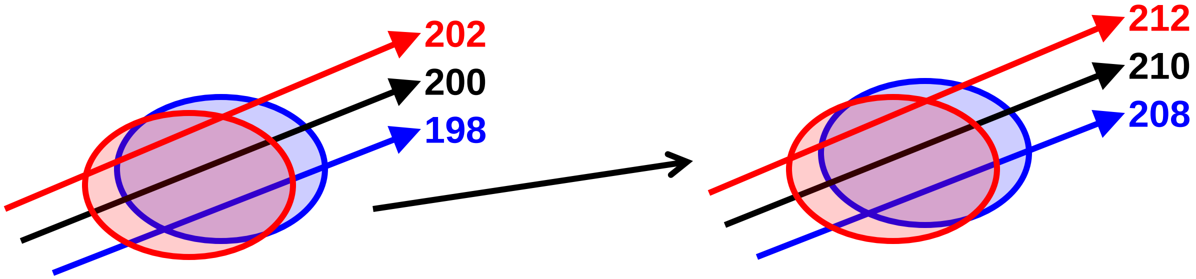
$$\rho_i \frac{D_i \mathbf{u}_i}{Dt} = -\nabla p_i + \sum_j A_{ij} \left(\mathbf{u}_j - \mathbf{u}_i \right)$$

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla$$

$$\frac{D_i}{Dt} = \frac{\partial}{\partial t} + \mathbf{u}_i \cdot \nabla$$

- **Ignoring inertial difference between species, we approximate**

$$\frac{D\mathbf{u}}{Dt} = \frac{D_i \mathbf{u}_i}{Dt}$$



Carrying on …

- Using $\frac{D_i \mathbf{u}_i}{Dt} \approx \frac{D\mathbf{u}}{Dt} = -\frac{1}{\rho}\nabla p$, we have

$$-\frac{\rho_i}{\rho}\nabla p = -\nabla p_i + \sum_j A_{ij}\left(\mathbf{u}_j - \mathbf{u}_i\right)$$

- After some algebra, we have the SM equation

$$\boxed{\sum_j \frac{z_i z_j}{D_{ij}}\left(\mathbf{u}_j - \mathbf{u}_i\right) = \underbrace{\nabla \frac{p_i}{p}}_{\text{ordinary diffusion}} + \underbrace{\left(z_i - y_i\right)\frac{\nabla p}{p}}_{\text{pressure diffusion}}}$$

$$D_{ij} \equiv \frac{p_i p_j}{p} A_{ij}, \quad z_i \equiv \frac{p_i}{p}, \quad y_i \equiv \frac{\rho_i}{\rho}$$

Momentum exchange (friction) coefficient A_{ij}

- **Can be obtained using the elementary kinetic theory**
  - Evaluation of the collision integral between species *i* and *j* using the Maxwell-Boltzmann distribution of the binary pair
  - Collision cross section provided by the interaction potential.

$$A_{ij} = A_{ji} = \frac{p}{p_i p_j} D_{ij} = \frac{16}{3} n_i n_j \mu_{ij} \Omega_{ij}^{(1)}(1,T)$$

$$\Omega_{ij}^{(1)}(n,T) = \frac{1}{2\sqrt{\pi}} \left(\frac{\mu_{ij}}{2k_B T} \right)^{\frac{2n+3}{2}} \int_0^\infty \exp\left(-\frac{\mu_{ij} v^2}{2k_B T} \right) v^{2n+3} Q_{ij}^{(1)}(v)\, dv$$

$$Q_{ij}^{(1)}(v) = 2\pi \int_0^\infty (1 - \cos\chi)\, b\, db$$

- **For hard-sphere,**

$$A_{ij} = \frac{8}{3} n_i n_j \sigma_{ij} \left(\frac{2\mu_{ij} k_B T}{\pi} \right)^{1/2}$$

Properties of SM equations

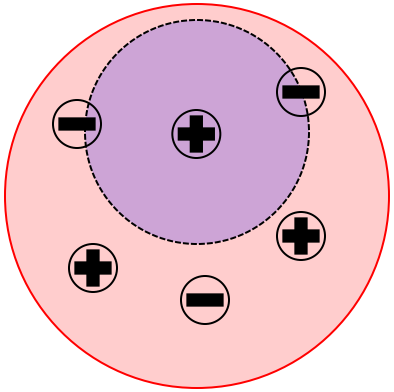
- **Only *N* - 1 SM equations are linearly independent**
  - Summing over *i* results in **0** = **0**
- **Nth condition provided by** $\sum_i \mathbf{J}_i = \sum_i \rho_i(\mathbf{u}_i - \mathbf{u}) = 0$
- **Mass conservation automatically satisfied**
- **Use binary diffusion coefficient, not multicomponent diffusion coefficient**
  - More convenient
- **Agrees exactly with the first-order Chapman-Enskog theory**
- **Thermal diffusion can be included (not shown here)**

Summary so far

- **Mass conservation must be satisfied**
  - Practice of solving diffusion equation for N - 1 species and obtaining Nth species diffusion flux using the mass conservation should be avoided
- **Multicomponent diffusion coefficient not convenient**
  - Local composition dependency
- **Approximations available for making Fick's law operate**
- **SM equations more convenient**
  - Binary diffusion coefficients
  - Mass conservation automatic
- **SM equation results agree exactly with the first order Chapman-Enskog theory**
- **Hydrodynamic theory for developing SM equation**
  - Provides framework for easier extension for additional physical effects.

Diffusion in plasmas

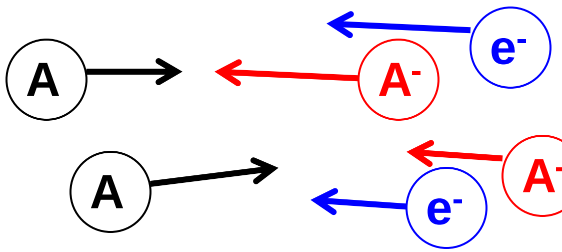
- **Charge neutrality needs be satisfied**
  - Not in Debye sphere or sheath
- **Ambipolar diffusion**
  - Light electrons try to outrun ions
  - Ions pull back electrons
  - Electrons pull ions forward, enhancing ion diffusion
  - I.e., electric field developed in plasma to keep charge neutrality
  - Electron and ion diffuse as pair
  - Zero electrical current



- **Charge neutrality still satisfied in the presence of electrical current**
- **Electron temperature often differs from heavy-particle temperature (two-temperature)**

Textbook description of ambipolar diffusion

- **Limited to three component plasmas**
  - Atom, ion, and electron
  - Diffusion between ion/electron pair and atom
- **Diffusion flux of ion and atom enhanced**



$$\mathbf{J}_I = -\frac{\rho_I \rho_A}{\rho z_I z_A} D_{IA} \left(1 + \frac{T_e}{T}\right) \nabla \frac{p_I}{p}$$

- **But this treatment is difficult to extend to two-temperature mixtures with arbitrary composition**

Hydrodynamic theory applied to plasma diffusion

- **Easier to include:**
  - Electromagnetic force
  - Two-temperature
  - Multicomponent
- **We start from (CGS unit)**

$$\rho_i \frac{D_i \mathbf{u}_i}{Dt} = -\nabla p_i + \sum_j A_{ij}\left(\mathbf{u}_j - \mathbf{u}_i\right) + \rho_i \mathbf{g} + \underbrace{\rho_i q_i \left(\mathbf{E} + \frac{1}{c}\mathbf{u}_i \times \mathbf{B}\right)}_{\text{New terms (Lorentz force)}}$$

$$\rho \frac{D\mathbf{u}}{Dt} = -\nabla p + \rho \mathbf{g} + \frac{1}{c}\mathbf{J}_q \times \mathbf{B}$$

- **Charge neutrality and current density**

$$\sum_i \rho_i q_i = 0, \qquad \mathbf{J}_q = \sum_i \rho_i q_i \mathbf{u}_i$$

Going through the same procedure,

- **The generalized Stefan-Maxwell equations given by**

$$\boxed{\sum_j \frac{z_i z_j}{D_{ij}}\left(\mathbf{u}_j - \mathbf{u}_i\right) + \frac{\rho_i q_i}{pc}\mathbf{u}_i \times \mathbf{B} = \nabla\frac{p_i}{p} + \left(z_i - y_i\right)\frac{\nabla p}{p} + \frac{y_i}{pc}\mathbf{J}_i \times \mathbf{B} - \frac{\rho_i q_i}{p}\mathbf{E}}$$

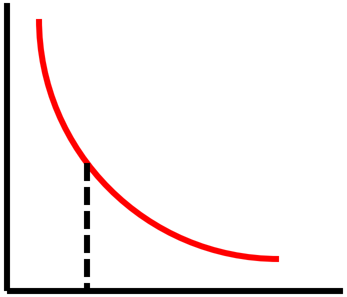
- **Each species allowed to have its own temperature**
  - Multi-T instead of 2-T
  - 2-T when all ion temperatures are the same.
- **Additional terms represent "forced diffusion" caused by electromagnetic forces**

A_{ij} for multitemperature mixture plasmas

- **Elementary kinetic theory generalized for multi-temperature mixtures**
  - Each ion species has its own temperature
  - J. M. Burger, Flow Equations for Composite Gases (Academic, NY, 1969).
- **Collision integrals evaluated using the effective pair temperature**

$$A_{ij} = A_{ji} = \frac{16}{3} n_i n_j \mu_{ij} \Omega_{ij}^{(1)}(1, T_{ij})$$

$$T_{ij} = \frac{m_i T_j + m_j T_i}{m_i + m_j}$$



- **For cut-off Coulomb potential**

$$A_{ij} = \frac{4}{3}\left(\frac{\pi \mu_{ij}}{2}\right)^{1/2} n_i n_j e_i^2 e_j^2 \left(k_B T_{ij}\right)^{-3/2} \ln\left(1 + \Lambda^2\right), \quad \Lambda = \frac{3 k_B T_{ij} R_D}{\left|e_i e_j\right|}$$

Determining $\mathbf{J}_q$, E, and B

- **It is necessary to determine additional unknowns: $\mathbf{J}_q$, E, and B**
- **So we have *N* + 3 unknowns B, E, $\mathbf{J}_q$, and $\mathbf{u}_i$**
- **Do we have *N* + 3 equations?**
  - N - 1 SM equations
  - B is determined by the Faraday's Law, $\nabla \times \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t}$
  - J_q obtained by Ampere's Law,

$$\nabla \times \mathbf{B} = \frac{4\pi}{c}\mathbf{J}_q + \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t}$$

  - Mass conservation,

$$\sum_i \mathbf{J}_i = \sum_i \rho_i \left(\mathbf{u}_i - \mathbf{u}\right) = \mathbf{0}$$

  - Current,

$$\mathbf{J}_q = \sum_i \rho_i q_i \mathbf{u}_i$$

- **Relationship between E and $\mathbf{J}_q$ is implicitly determined in multicomponent MHD. I.e., Ohm's law is NOT an independent constitutive relation. It is a consequence of species diffusion flux.**

Simplification for small m_e

- **System of equations is stiff – difficult to solve numerically**
- **For electrons, SM equation becomes**
  - "Ideal" MHD with no electrical resistance

$$\mathbf{E} = \frac{1}{\rho_i q_i} \nabla p_e + \frac{1}{c} \mathbf{u}_e \times \mathbf{B}$$

- **E eliminated from SM equations as**

$$\sum_j \frac{z_i z_j}{D_{ij}} \left(\mathbf{u}_j - \mathbf{u}_i \right) + \frac{\rho_i q_i}{pc} \left(\mathbf{u}_i - \mathbf{u}_e \right) \times \mathbf{B} = \nabla \frac{p_i}{p} + \left(z_i - y_i \right) \frac{\nabla p}{p} + \frac{y_i}{pc} \mathbf{J}_i \times \mathbf{B} - \frac{\rho_i q_i}{\rho_e q_e} \frac{\nabla p_e}{p}$$

- **u_e is obtained from** $\mathbf{J}_q = \sum_i \rho_i q_i \mathbf{u}_i$
- **Ambipolar diffusion described by setting** $\mathbf{J}_q = \mathbf{0}, \quad \mathbf{B} = \mathbf{0}$

Summary

- **Multicomponent diffusion formulation in the framework of Stefan-Maxwell equations.**
- **SM equations derived using hydrodynamic theory of diffusion**
- **Ease of adding physical processes makes it possible to develop multicomponent diffusion in two temperature plasmas**
  - Charge neutrality and ambipolar diffusion
  - Electromagnetic forces
  - Simplification due to small electron mass
- **Elementary kinetic theory used for evaluation of A_{ij}**
- **Thermal diffusion can be included**
- **Consequences in energy equation must not be neglected**
  - Frictional dissipation and Joule heating
  - Enthalpy diffusion

Take home messages

- **Mass conservation must be satisfied**
  - Not usually satisfied by Fick's law when $N > 2$
- **Multicomponent diffusion coefficients used by Fick's law are difficult to deal with**
- **SM equations preferred over Fick's law**
  - Mass conservation is a part of the equation set, so mass conservation is automatic
  - Binary diffusion coefficient used
- **Diffusion in plasmas have additional requirements**
  - Charge neutrality
  - Ambipolar diffusion
- **SM equations provide physically intuitive framework for extension**
  - Forced diffusion
  - Multi-temperature mixtures